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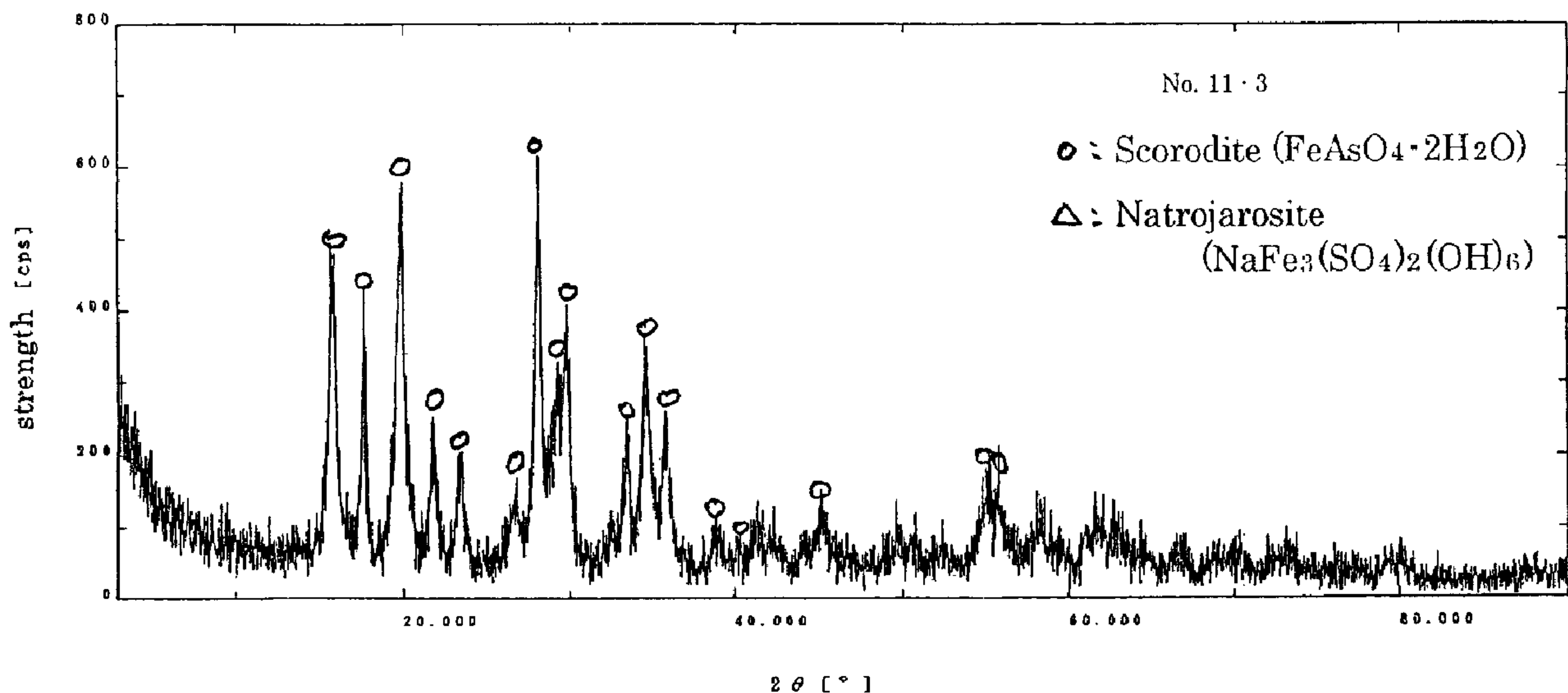
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(54) Titre : PROCEDE DE FABRICATION DE LA SCORODITE

(54) Title: METHOD FOR MANUFACTURING SCORODITE



(57) Abrégé/Abstract:

The present invention provides a method for manufacturing scorodite in which scorodite may be obtained at high production efficiency and a high As concentration ratio. The present invention provides a method for manufacturing crystalline scorodite from acidic aqueous solution containing pentavalent As and trivalent Fe, the method comprising a step for adding a basic sodium compound to the acidic aqueous solution such that the sodium concentration in the acidic aqueous solution becomes larger than 0 g/L and equal to or less than 4 g/L.

ABSTRACT

The present invention provides a method for manufacturing scorodite in which scorodite may be obtained at high production efficiency and a high As concentration ratio. The present invention provides a method for manufacturing crystalline scorodite from acidic aqueous solution containing pentavalent As and trivalent Fe, the method comprising a step for adding a basic sodium compound to the acidic aqueous solution such that the sodium concentration in the acidic aqueous solution becomes larger than 0 g/L and equal to or less than 4 g/L.

Method for Manufacturing Scorodite

FIELD OF THE INVENTION

5 **[0001]** The present invention relates to a method for manufacturing scorodite. In particular, the invention relates to a method for manufacturing scorodite from electrolytically precipitated copper produced in copper smelting process.

BACKGROUND OF THE INVENTION

10 **[0002]** Various impurities are contained in copper ore, and one of the impurities is arsenic (As). While most of arsenic (As) is evaporated and separated by a high temperature during a dry process of the copper smelting, it is partially entrained in crude copper and carried into the subsequent copper electrorefining process.

Part of As contained in the crude copper (copper anode) is eluted into
15 electrolytic solution, and the remaining undissolved As is mixed in anode slime deposited on the bottom of an electrolytic tank. In addition, since the amount of copper eluted from the anode is generally larger than that of copper deposited on the cathode, the copper concentration will increase gradually in the electrolytic solution. Therefore, a part of the electrolytic solution is extracted into another electrolytic tank to
20 control the quality of the electrolytic solution. Decoppering electrolysis is conducted to the extracted electrolytic solution to separate and recover Cu and impurities such as As by precipitating them on the cathode or depositing them on the bottom of the electrolysis bath. In this technical field, the substances deposited on the bottom of the electrolytic tank and those precipitated on the cathode are called as "electrolytically
25 precipitated copper".

[0003] Electrolytically precipitated copper is typically fed back to the copper smelting process. For this purpose, impurities such as As should be desirably removed from the electrolytically precipitated copper. In addition, As in itself can be used as valuable material. Accordingly, there is a need for a technology to separate and
5 recover As from electrolytically precipitated copper with high grade. In this regard, Japanese unexamined patent publication No. 6-279879 discloses a method comprising adding electrolytically precipitated copper to sulfuric acid solution so that leaching reaction occurs and then separating sulfuric acid-leached solution containing As and Cu from leaching residue containing Bi and Sb. The publication states in the examples
10 section that electrolytically precipitated copper was added to 100 g/L sulfuric acid solution (the pH is speculated to be about -0.3.) to cause the sulfuric acid leaching.

[0004] Furthermore, it has been known that crystallization of scorodite ($\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}$), which is an iron-arsenic compound, is effective in fixing arsenic. Crystalline scorodite is chemically stable, and suitable for long-term storage. On the
15 other hand, amorphous scorodite is not stable, therefore not suitable for long-term storage.

[0005] For example, Japanese patent No. 3,756,687 discloses a method for removing and fixing arsenic from solution containing arsenic and non-ferrous metal component including copper and/or zinc. The method comprises a first step of adding
20 iron (II) solution and/or iron (III) solution to the arsenic-containing solution for reaction at 120 °C or higher to form scorodite having stable crystallinity as an iron-arsenic compound and then recovering scorodite containing non-ferrous metal components such as copper from the arsenic-containing solution by solid-liquid separation, and a second step of adding water to the obtained scorodite containing non-ferrous metal components

such as copper for repulping so that the non-ferrous metal components such as copper is dissolved into the solution and separated from the scorodite.

The patent states that in this way arsenic can be removed and fixed as stable crystalline scorodite without losing valuable metals such as copper.

5 **[0006]** Furthermore, Japanese unexamined patent publication No. 2005-161123 discloses a method for removing arsenic from soot containing arsenic. The method comprises a leaching step for leaching arsenic from the arsenic-containing soot with acid solution, a precipitation reaction step for precipitating amorphous iron arsenate by mixing iron ion-containing acidic aqueous solution in the leached solution,
10 and a crystallization step for crystallizing the amorphous iron arsenate by heating the mixed solution. The crystallized iron arsenate is removed by filtering the mixed solution.

The publication states that the method can remove arsenic from soot very easily since it needs no additional processes, such as pH adjustment, once the iron
15 ion-containing acidic aqueous solution is mixed in the leached solution.

Furthermore, it states in the embodiment section that sulfuric acid solution (concentration is 0.2 mol/L, i.e., pH is about 0.4) was used to leach arsenic from soot, and the pH of both the leached solution and the iron ion-containing acidic aqueous solution (ferric sulfate) was 1.0 to 1.5.

20

PROBLEMS TO BE SOLVED BY THE INVENTION

[0007] Even if crystalline scorodite was formed under the condition stated in Jpn. pat. No. 3,756,687 or Jpn. pat. pub. No. 2005-161123, highly concentrated As could not be obtained in some cases. In particular, although Jpn. pat. pub. No.

2005-161123 states that the proper pH for forming scorodite is 1.0 to 1.5, the formation of scorodite was sometimes insufficient and As concentration ratio thus decreased even though the pH was adjusted to the above range.

Therefore, the object of the present invention is to provide a method for
5 manufacturing scorodite in which scorodite may be obtained at high production efficiency and a high As concentration ratio.

MEANS FOR SOLVING THE PROBLEM

[0008] In the manufacture of scorodite from electrolytically precipitated
10 copper, components such as Bi and Sb should desirably be removed by sulfuric acid leaching in advance to facilitate the separation and recovery of valuable material. However, since sulfuric acid concentration used for the sulfuric acid leaching is often adjusted to higher level for the sake of better leaching efficiency, the pH of resulting sulfuric acid-leached solution may become less than 1.0. In such cases, alkali is added
15 as appropriate to adjust the pH to 1.0 to 1.5, which pH range is appropriate for forming crystalline scorodite. However, such alkaline component forms sulfate, hampering the formation of crystalline scorodite or forming together with crystalline scorodite, thus decreasing the arsenic concentration ratio.

[0009] The inventors have found out that a sodium compound is effective as
20 the alkali for pH adjustment. That is, when a sodium compound is used as the alkali, it does not hamper the formation of crystalline scorodite until it exceeds a certain amount. To be more specific, we have found out that the synthesis of crystalline scorodite is hardly hampered when the sodium concentration in the reaction medium is 4 g/L or less. The present invention has been made based on the aforementioned findings.

[0010] Accordingly, in one aspect, the invention is a method for manufacturing crystalline scorodite from acidic aqueous solution containing pentavalent As and trivalent Fe, the method comprising a step for adding a basic sodium compound to the acidic aqueous solution such that the sodium concentration in the acidic aqueous solution becomes larger than 0 g/L and equal to or less than 4 g/L.

[0011] In one embodiment of the invention, the basic sodium compound is at least one compound selected from the group consisting of sodium carbonate, sodium hydroxide, and sodium hydrogen carbonate.

[0012] In another embodiment of the invention, the pH of the acidic aqueous solution is less than 1.0 before the addition of the basic sodium compound and 1.0 to 1.5 after the addition.

[0013] In a further embodiment of the invention, the trivalent Fe is provided as ferric sulfate.

[0014] In a further embodiment of the invention, the acidic aqueous solution is sulfuric acid-leached solution from electrolytically precipitated copper.

ADVANTAGEOUS EFFECT OF THE INVENTION

[0015] The present invention prevents the formation of by-products during the crystalline scorodite synthesis, thereby enabling the selective scorodite synthesis. Therefore, it enables, for example, to fix arsenic from electrolytically precipitated copper at a high concentration ratio.

BRIEF DESCRIPTION OF THE DRAWINGS

[0016] Fig. 1 shows the XRD of scorodite crystal in Example 1 of the invention.

[0017] Fig. 2 shows the XRD of scorodite crystal in Example 2 in of the invention.

5 [0018] Fig. 3 shows the XRD of scorodite crystal in Comparative Example 1 of the invention.

[0019] Fig. 4 shows the XRD of scorodite crystal in Comparative Example 2 of the invention.

[0020] Fig. 5 shows the XRD of scorodite crystal in Comparative Example 3
10 of the invention.

BEST MODE FOR CARRYING OUT THE INVENTION

[0021] As stated above, the invention is characterized by the step for adding a basic sodium compound to acidic aqueous solution containing pentavalent As and
15 trivalent Fe such that the sodium concentration in the acidic aqueous solution becomes larger than 0 g/L and equal to or less than 4 g/L in the manufacture of crystalline scorodite from the acidic aqueous solution.

[0022] The pentavalent As may be provided, for example, in the form of arsenic acid (H_3AsO_4), and the trivalent Fe may be provided, for example, in the form of
20 iron oxide, iron sulfate, iron chloride and iron hydroxide. The acidic aqueous solution may be provided, for example, as hydrochloric acid acidity solution, sulfuric acid acidity solution, perchloric acid acidity solution, or the like. As a typical example, the pentavalent As exists in the form of arsenic acid (H_3AsO_4) in sulfuric acid-leached solution obtained by the sulfuric acid leaching of electrolytically precipitated copper.

[0023] The sulfuric acid leaching of electrolytically precipitated copper can be performed, for example, in the following manner.

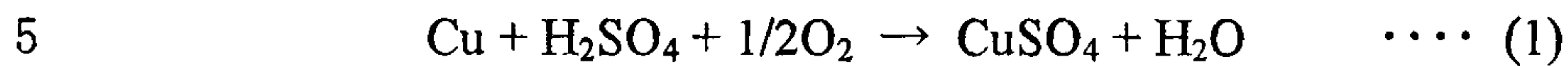
Firstly, electrolytically precipitated copper is optionally water-washed. In the water-washing, the electrolytically precipitated copper may be repulped with
5 water and stirred for 0.5 to 6 hours to dissolve the components of the electrolytic solution (including copper sulfate, Ni and Fe, which were deposited during the manufacture of the electrolytically precipitated copper, and minute amounts of Ni, Fe and the like contained in the electrolytically precipitated copper, and then the resulting slurry may be filtered and separated into solid and liquid. This process enables to
10 separate most part of Fe and Ni from the electrolytically precipitated copper.

However, the primary purpose of this process is to determine the amount of zero-valent copper, which is water-insoluble, in the total copper amount, i.e., the amount of copper excluding copper sulfate, in the electrolytically precipitated copper in order to more precisely determine the amount of sulfuric acid necessary for sulfuric acid
15 leaching performed in the subsequent process. This process may not be necessary when minor elements such as Ni and Fe are not of particular concern, when the amount of copper sulfate is already known, or when the amount of the electrolytic solution introduced into the electrolytically precipitated copper is small.

[0024] After the optional water-washing, the sulfuric acid leaching is
20 performed by feeding an oxygen-containing gas into the electrolytically precipitated copper in the sulfuric acid acidity solution and stirring the solution under temperature and time conditions sufficient to oxidize As component contained in the electrolytically precipitated copper to pentavalence. Then, it is separated into solid, i.e., a leaching

residue containing Sb and Bi components, and liquid, i.e., sulfuric acid-leached solution containing pentavalent As component.

[0025] The leaching reaction occurred in this process is generally represented by the following formula, and Cu is oxidized to Cu^{2+} and As is oxidized to As^{5+} .



The usage of sulfuric acid is preferably 1.0 to 1.2 equivalents based on Cu. Below 1.0 equivalents, the leached solution becomes a weak acid, thereby forming precipitates such as Cu_3AsO_4 and decreasing the leaching ratio of Cu and As. Above 1.2 equivalents, the usage of sulfuric acid becomes large although there is no adverse effect on the leaching ratio of Cu and As. Although there is no particular restriction on the concentration of Cu and As in the sulfuric acid solution, the leaching ratio will decrease if the concentration exceeds the solubility. Therefore, the concentration of Cu and As is preferably no larger than the solubility of Cu^{2+} and As^{5+} .

15 Furthermore, although the suitable pH for the formation of crystalline scorodite is 1.0 to 1.5, lower sulfuric acid concentration tends to decrease the efficiency of the sulfuric acid leaching, i.e., the recovery ratio of copper and arsenic. Therefore, the sulfuric acid concentration used in the sulfuric acid leaching is preferably determined such that the pH becomes less than 1. Therefore, in such case, the pH of
20 the sulfuric acid-leached solution often becomes less than 1. In addition, even if the pH of the sulfuric acid-leached solution is equal to or more than 1, the trivalent iron added for the scorodite synthesis is preferably supplied in the form of acidic aqueous solution as described later. For example, the pH of ferric sulfate solution and poly

ferric sulfate solution is around 0.6. In this case, the pH often becomes less than 1 upon the addition of the trivalent iron.

[0026] The sulfuric acid leaching may be conducted with stirring for instance at 70 to 95 °C for 4.5 to 11 hours, preferably at 80 to 95 °C for 7 to 11 hours to oxidize As to pentavalence. Since the sulfuric acid leaching is exothermic reaction, it can be done without the application of external heat. The stirring may be conducted for a longer period, and the actual time may be determined as appropriate based on cost and efficacy.

To improve the oxidation efficiency of As, the bubbles of the introduced oxygen-containing gas should be smaller in size, and enough amount of the gas (e.g., 10 equivalents of oxygen based on copper per 7 hours) should be supplied. Therefore, stronger stirring is preferable. For example, the feeding and/of stirring of the oxygen-containing gas is preferably performed by jet injection. The aforementioned value applied to a process using jet injection (Jet Ajiter™). Therefore, when using a conventional agitator having turbine blades, twice the reaction time or more is necessary even if 3.5 times the amount of the oxygen-containing gas or more is introduced. By controlling the valence of As at this stage, the scorodite formation at later stage becomes easier. Cu^{2+} also has the effect of accelerating the As oxidation.

[0027] There is no particular restriction on the type of oxygen-containing gas unless it gives any adverse effect on the aforementioned reaction. For example, pure oxygen or a mixture of oxygen and inert gas can be used. It is preferably air in terms of handling and cost.

[0028] Acidic aqueous solution containing pentavalent As and trivalent Fe may be obtained by adding trivalent iron to the sulfuric acid-leached solution of

electrolytically precipitated copper. In this case, examples of the trivalent iron include iron oxide, iron sulfate, iron chloride and iron hydroxide. However, the trivalent iron should desirably be supplied in the form of acidic aqueous solution since in terms of reacting in aqueous solution. Furthermore, since the most effective way is to return
 5 the post-deferrization solution to the electrolytic solution used in the electrical smelting, it is preferably supplied in the form of ferric sulfate ($\text{Fe}_2(\text{SO}_4)_3$) aqueous solution. Poly ferric sulfate, which is used in drainage treatment, can be also used.

The amount of trivalent iron necessary to remove As is equal to or larger than 1.0 equivalent based on As, and is preferably 1.1 to 1.5 equivalents in terms of
 10 cost.

[0029] A basic sodium compound is added to the acidic aqueous solution to achieve a proper pH value for the scorodite synthesis. The addition amount is determined such that the sodium concentration in the solution becomes larger than 0 g/L and equal to or less than 4 g/L, and preferably larger than 0 g/L and equal to or less than
 15 2.5 g/L. While the adjustment of pH value cannot be made unless the sodium compound is added, addition of more than 4 g/L of the sodium compound tends to form Natrojarosite ($\text{NaFe}_3(\text{SO}_4)_2(\text{OH})_6$), decreasing the arsenic concentration ratio.

There is no particular restriction on the addition timing of the sodium compound provided that it is added with a proper pH value. It may be added before
 20 the synthesis (i.e., before the heating) or during the heating. However, it is preferably added before the heating for the sake of the effective synthesis of stable scorodite.

[0030] Examples of the basic sodium compound include, but not limited to, sodium hydroxide, sodium carbonate, and sodium hydrogen carbonate. As a typical example, sodium hydroxide may be used. Incidentally, alkalis such as potassium

hydroxide, calcium hydroxide and calcium carbonate may be regarded as the potential additive. However, when potassium hydroxide is used, it is not only undesirable in terms of cost, but also tends to form precipitate of jarosite ($\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6$) as a by-product. Furthermore, calcium hydroxide and calcium carbonate are also
5 undesirable since they easily form a calcium sulfate (gypsum) precipitation and decrease the arsenic concentration ratio.

[0031] The pH of the acidic aqueous solution after the addition of the basic sodium compound is preferably 0.3 to 2.2. When the pH becomes less than 0.3, the solubility of crystalline scorodite increases rapidly, thereby hampering the crystalline
10 scorodite formation. Furthermore, when the pH is greater than 2.2, the added iron precipitates as iron hydroxide, resulting in ineffective use of iron for the scorodite synthesis. The effectiveness of the crystalline scorodite formation becomes higher especially when the pH of the acidic aqueous solution is 1.0 to 1.5.

[0032] Crystalline scorodite can be formed by, for example, heating the acidic
15 aqueous solution at 60 to 95 °C under the atmospheric pressure. For example, 8 to 72 hours of reaction will form a sufficient amount of crystalline scorodite. Since As has been oxidized to pentavalence, it reacts with the trivalent iron at high efficiency and forms crystalline scorodite. Crystalline scorodite is chemically stable, and suitable for long-term storage. By separating the product into solid and liquid, i.e., a residue
20 containing crystalline scorodite and a post-dearsenic solution, arsenic can be recovered as scorodite.

EXAMPLES

[0033] Examples in accordance with the invention will be explained hereinafter for the better understanding of the invention and advantages thereof. However, the invention is not limited to the examples.

[0034]

5 Example 1

Ferric sulfate solution (formed by dissolving 57.3 g of ferric sulfate reagent (n hydrate, iron(III) content was about 21.3 %) in warm water; 2.0 equivalents of iron(III) based on arsenic) was added to 23.7 g of 60 % arsenic acid solution manufactured by Wako Pure Chemical Industries, Ltd. (the content of arsenic was 10 33.8 %). Then, the solution was diluted with water to 640 mL. Since the pH of the mixed solution was 0.75, 17 mL of 25 % NaOH solution was added to adjust the pH to 1.0. Na concentration in the mixed solution was 3.8 g/L (measured by an ICPAES analyzer, Model No. SPS3100 available from Seiko Instruments Inc.). Then, the solution was heated to 95 °C, during which the amount of the solution was concentrated 15 to 640 mL, and the scorodite synthesis was conducted for 24 hours. During the heating, the amount of the solution was kept to 640 mL by adding water as appropriate to prevent the excessive decrease of the solution due to evaporation. Although the reaction did not progress immediately after the mixture of the arsenic acid solution and ferric sulfate solution at room temperature, the precipitation of scorodite was observed 20 at around 60 °C as the mixture was heated. After the synthesis of scorodite, the scorodite crystal was filtered and separated into solid and liquid. The scorodite crystal was washed with water, and the wash water was added to the post-filtration solution. Table 1 shows the amount of the obtained scorodite crystal and post-crystal filtration solution. The arsenic content in the scorodite was 30% and high arsenic concentration

ratio was obtained. Fig. 1 shows the XRD of the obtained scorodite. Arsenic elution was little, and crystalline scorodite, which is considered to be stable, was obtained. The crystallization of Natrojarosite was not observed.

Incidentally, the arsenic elution from the scorodite obtained by this synthesis was 0.99 mg/L (TCLP, acetic acid buffer solution having the pH of 5 was used), and therefore it was confirmed that the arsenic was stable. This result also shows that the obtained scorodite was crystalline.

[0035]

Table 1

arsenic acid solution				ferric sulfate (n hydrate)			
amount(g)	23.7			amount(g)	57.3		
	content(%)	number of moles(mol)	(molecular weight)		content(%)	number of moles(mol)	(molecular weight)
T-As	33.8	0.107	74.92	T-As	0.0		
T-Fe	0.0			T-Fe	21.3	0.218	55.85
				S	18.3	0.327	32.070
				Na			

adjusting pH to 1.0 with 17 mL of 25% NaOH solution

scorodite synthesis pH=1.0, 95°C, 24hrs			
amount(ml)	640		
	content(%)	number of moles(mol)	(molecular weight)
T-As	12.5	0.107	74.92
T-Fe	19.0	0.218	55.85
S	16.4	0.327	32.070
Na	3.8	0.106	22.990

scorodite crystal			
amount(Dg)	15.9		
	content(%)	number of moles(mol)	(molecular weight)
T-As	30.0	0.064	74.92
T-Fe	25.0	0.071	55.85
S	1.4	0.007	32.070
Na	0.0	0.000	22.990

post filtration solution			
amount(ml)	1380		
	content(%)	number of moles(mol)	(molecular weight)
T-As	2.28	0.042	74.92
T-Fe	6.67	0.165	55.85
S		0.000	32.070
Na		0.000	22.990

10

[0036]

Example 2

After 54.0 mL of ferric sulfate manufactured by Nittetsu mining Co., Ltd.

(referred hereinafter as poly iron) was added to 370 mL of the sulfuric acid-leached solution from electrolytically precipitated copper (the manufacturing method will be explained later), the solution was diluted with water to 650 mL (1.5 equivalents of iron(III) based on arsenic). Since the pH of the mixed solution was 0.97, 5 mL of NaOH solution having the concentration of 40 g/L was added to adjust the pH to 1.0. Na concentration in the mixed solution was 0.15 g/L (measured by an ICPAES analyzer, Model No. SPS3100 available from Seiko Instruments Inc.). Then, the solution was heated to 95 °C, during which the amount of the solution was concentrated to 650 mL, and the scorodite synthesis was conducted for 24 hours. During the heating, the amount of the solution was kept to 650 mL by adding water as appropriate to prevent the excessive decrease of the solution due to evaporation. Although the reaction did not progress immediately after the mixture of the arsenic acid solution and ferric sulfate solution at room temperature, the precipitation of scorodite was observed at around 40 °C as the mixture was heated. After the scorodite synthesis, the scorodite crystal was filtered and separated into solid and liquid. The scorodite crystal was washed with water, and the wash water was added to the post-filtration solution. Table 2 shows the amount of the obtained scorodite crystal and post-crystal filtration solution. The arsenic content in the scorodite was 31% and the arsenic concentration ratio was high. Fig. 2 shows the XRD of the obtained scorodite crystal. Crystalline scorodite, which is believed to shows little arsenic elution and to be stable, was obtained. The crystallization of Natrojarosite was not observed.

[0037] Incidentally, arsenic elution from the scorodite obtained by this synthesis was 0.2 mg/L (TCLP, acetic acid buffer solution having the pH of 5 was used), therefore it was confirmed that the arsenic was stable. The result also shows that the

obtained scorodite was crystalline.

[0038]

Table 2

sulfuric acid leaching post-filtration solution

pH1.56 As : 7g

amount(ml)	370		
	content(%)	number of moles(mol)	(molecular weight)
As	19.00	0.094	74.92
Fe	0.00	0.000	55.85
Cu	31.00	0.180	63.55
Sb	0.35	0.001	121.76
Bi	0.04	0.000	208.98
Ni	0.11	0.001	58.69
Pb	0.02	0.000	207.21
Ca	0.00	0.000	40.08
SiO ₂		0.000	60.09
S	14.00	0.162	32.07
H ₂ SO ₄	6.5	0.024	98.07

poly ferric sulfate Fe/As=1.5 (actual value 1.54)

amount(ml)	54.0		
	content(%)	number of moles(mol)	(molecular weight)
T-As	0.0		74.92
T-Fe	150.0	0.145	55.85
T-Cu			63.55
Sb			121.76
Bi			208.98
Ni			58.69
Pb			207.21
Ca	0.0	0.000	40.08
SiO ₂			60.09
S	120.0	0.202	32.07
H ₂ SO ₄			98.07

adding 5 mL of 40g/L NaOH solution

scorodite synthesis pH=1.0, 95°C, 24hrs

amount(ml)	650		
	content(%)	number of moles(mol)	(molecular weight)
As	10.82	0.094	74.92
Fe	12.46	0.145	55.85
Cu	17.65	0.180	63.55
Sb	0.20	0.001	121.76
Bi	0.02	0.000	208.98
Ni	0.06	0.001	58.69
Pb	0.01	0.000	207.21
Ca	0.00	0.000	40.08
SiO ₂	0.00	0.000	60.09
S	17.94	0.364	32.07
Na	0.15	0.004	22.99
H ₂ SO ₄	3.67	0.024	98.07

pH1.0 ORP625mV

scorodite crystal

amount(Dg)	25.1		
	content(%)	number of moles(mol)	(molecular weight)
As	31.00	0.10	74.92
Fe	24.00	0.11	55.85
Cu	1.10	0.00	63.55
Sb	0.46	0.00	121.76
Bi	0.01	0.00	208.98
Ni		0.00	58.69
Pb	0.01	0.00	207.21
Ca	0.00		40.08
SiO ₂		0.00	60.09
S	1.50	0.01	32.07
Na	0.00	0.000	22.99

post-filtration solution

amount(ml)	1660		
	content(%)	number of moles(mol)	(molecular weight)
As	0.11	0.00	74.92
Fe	1.80	0.05	55.85
Cu	7.00	0.18	63.55
Sb	0.01	0.00	121.76
Bi	0.00	0.00	208.98
Ni		0.00	58.69
Pb	0.00	0.00	207.21
Ca	0.01	0.00	40.08
SiO ₂		0.00	60.09
S	6.50	0.34	32.07
Na	0.030	0.002	22.99

[0039]

[Method for manufacturing sulfuric acid-leached solution from electrolytically

precipitated copper]

A method for manufacturing the electrolytically precipitated copper, which was used in Example 2, is explained hereinafter.

(1) Water-washing process of electrolytically precipitated copper

5 2000 g (wet weight) of electrolytically precipitated copper was repulped with 5000 mL of water and stirred for four hours to dissolve the components of the electrolytic solution (including copper sulfate, Ni and Fe) which were deposited during the manufacture of the electrolytically precipitated copper. The slurry was then filtered and separated into solid and liquid. The obtained residue was dried, and used
10 for sulfuric acid leaching in the next step. The weight of the dried residue was 1423 g. Table 3 shows the analytical values. Incidentally, the purpose of this process is to determine the amount of zero-valent copper, which is water-insoluble, in the total copper amount, i.e., the amount of copper excluding copper sulfate, in the electrolytically precipitated copper in order to more precisely determine the amount of
15 sulfuric acid necessary for sulfuric acid leaching performed in the subsequent process. This process may not be necessary when the amount of copper sulfate is already known, or when the amount of the electrolytic solution introduced into the electrolytically precipitated copper is small.

[0040]

Table 3

electrolytically precipitated copper (Wet)

amount(Wg)	2000.0		
	content(%)	number of moles(mol)	(molecular weight)
H ₂ O	11.33		

electrolytically precipitated copper (Dry)

amount(Dg)	1773.4		
	content(%)	number of moles(mol)	(molecular weight)
As	28.0	6.63	74.92
Fe	0.04	0.01	55.85
Cu	41.0	11.44	63.55
Sb	2.10	0.31	121.76
Bi	2.00	0.17	208.98
Ni	1.00	0.30	58.69
Pb	1.90	0.16	207.21
Ca	0.00	-	40.08
Si	0.00	0.00	60.09
S	3.60	1.99	32.07

electrolytically precipitated copper (Dry)
water washing : 5 L, 4hrs

amount(Dg)	1423.0		
	content(%)	number of moles(mol)	(molecular weight)
As	34.00	6.46	74.92
Fe	0.00	0.00	55.85
Cu	48.00	10.75	63.55
Sb	2.60	0.30	121.76
Bi	2.50	0.17	208.98
Ni	0.25	0.06	58.69
Pb	2.80	0.19	207.21
Ca	0.03	-	40.08
Si	0.01	0.00	60.09
S	0.43	0.19	32.07

pH0.70

post-filtration liquid (electrolytically
precipitated copper pre-treated solution)

amount(ml)	5900		
	content(%)	number of moles(mol)	(molecular weight)
As	4.90	0.39	74.92
Fe	0.15	0.02	55.85
Cu	5.20	0.48	63.55
Sb	0.02	0.00	121.76
Bi	0.05	0.00	208.98
Ni	2.40	0.30	58.69
Pb	0.01	0.00	207.21
Ca	0.00	-	40.08
SiO ₂		0.00	60.09
S	11.00	0.66	98.07

[0041]

5 (2) Sulfuric acid leaching of electrolytically precipitated copper

To 185 g (dry weight) of the water-washed electrolytically precipitated copper was added 145g of 98 % concentrated sulfuric acid (1.04 equivalents based on the amount of copper contained in the electrolytically precipitated copper), and then

water was added such that the amount of the slurry became 1850 mL (the slurry concentration was 100 g/L). The leaching was performed with feeding air at the flow rate of 700 mL/minute and stirring for 7 hours. To improve the reaction efficiency, the bubbles of the introduced air should be smaller in size. Therefore, Jet Ajiter
5 (manufactured by Shimazaki Mixing Equipment Co., Ltd.) was used for the air feeding and stirring. Incidentally, the liquid temperature was not controlled. However, since the sulfuric acid leaching is exothermic reaction, the liquid temperature rose to 88 °C after 3 hours from the start of the leaching, then gradually decreased, and was 70 °C after 7 hours. After the sulfuric acid leaching, the leached components were filtered
10 and separated into solid and liquid. The residue was washed with water, and the wash water was added to the sulfuric acid-leached solution. Table 4 shows the amount of the obtained sulfuric acid-leached solution and sulfuric acid leaching residue.

[0042]

Table 4

electrolytically precipitated copper water
washing residue (Dry)

amount(Dg)	185		
	content(%)	number of moles(mol)	(molecular weight)
As	34.0	0.840	74.92
Fe	0.0	-	55.85
Cu	48.0	1.397	63.55
Sb	2.6	0.040	121.76
Bi	2.5	0.022	208.98
Ni	0.3	0.008	58.69
Pb	2.8	0.025	207.21
Ca	0.0	-	40.08
SiO ₂	0.0	0.000	60.09
S	0.4	0.025	32.07
H ₂ SO ₄	-	-	98.07

98% sulfuric acid (addition amount is 1.04
equivalents based on copper)

amount(g)	145.0		
	content(%)	number of moles(mol)	(molecular weight)
As	-	-	74.92
Fe	-	-	55.85
Cu	-	-	63.55
Sb	-	-	121.76
Bi	-	-	208.98
Ni	-	-	58.69
Pb	-	-	207.21
Ca	-	-	40.08
SiO ₂	-	-	60.09
S	-	-	32.07
H ₂ SO ₄	98.0	1.45	98.07

sulfuric acid leaching : 100g/l, 70°C, 7hrs, air
700ml/min (Jet Agiter)

amount(mg)	1850		
	content(%)	number of moles(mol)	(molecular weight)
As	34.0	0.840	74.92
Fe	-	-	55.85
Cu	48.0	1.397	63.55
Sb	2.6	0.040	121.76
Bi	2.5	0.022	208.98
Ni	0.3	0.008	58.69
Pb	2.8	0.025	207.21
Ca	-	-	40.08
SiO ₂	0.0	0.000	60.09
S	87.7	1.478	32.07
H ₂ SO ₄	77.0	1.453	98.07

pH1.56 ORP 421mV

sulfuric acid leaching residue (Dry)

amount(Dg)	33.9		
	content(%)	number of moles(mol)	(molecular weight)
As	19.00	0.086	74.92
Fe	0.02	-	55.85
Cu	13.00	0.069	63.55
Sb	11.00	0.031	121.76
Bi	15.00	0.024	208.98
Ni	0.02	0.000	58.69
Pb	12.00	0.020	207.21
Ca	0.02	-	40.08
Si	0.23	0.001	60.09
S	1.70	0.018	32.07
H ₂ SO ₄	-	-	98.07

post-sulfuric acid leaching and filtration solution

amount(ml)	2855		
	content(%)	number of moles(mol)	(molecular weight)
As	19.00	0.72	74.92
Fe	0.00	0.00	55.85
Cu	31.00	1.39	63.55
Sb	0.35	0.01	121.76
Bi	0.04	0.00	208.98
Ni	0.11	0.01	58.69
Pb	0.02	0.00	207.21
Ca	0.00	0.00	40.08
SiO ₂	-	0.00	60.09
S	14.00	1.246	32.07
Na	0.25	0.01	98.07

[0043]

Comparative Example 1

Ferric sulfate solution (formed by dissolving 57.3 g of Ferric sulfate reagent (n hydrate, iron(III) content was about 21.3 %) in warm water, 2.0 equivalents
5 of iron(III) based on arsenic) was added to 23.7 g of 60 % arsenic acid solution manufactured by Wako Pure Chemical Industries, Ltd. (the content of arsenic was 33.8 %). Then, the solution was diluted with water to 640 mL. Since the pH of the mixed solution was 0.75, 46 mL of 25 % NaOH solution was added to adjust the pH to 1.5. Na concentration in the mixed solution was 10.3 g/L (measured by an ICPAES
10 analyzer, Model No. SPS3100 available from Seiko Instruments Inc.). Then, the solution was heated to 95 °C, during which the amount of the solution was concentrated to 640 mL, and the scorodite synthesis was conducted for 24 hours. During the heating, the amount of the solution was kept to 640 mL by adding water as appropriate to prevent the excessive decrease of the solution due to evaporation. Although the
15 reaction did not progress immediately after the mixture of the sulfuric acid-leached solution and ferric sulfate solution at room temperature, yellow precipitation was observed at around 60 °C as the mixture was heated. After the scorodite synthesis, the obtained crystal was filtered and separated into solid and liquid. The crystal was washed with water, and the wash water was added to the post-filtration solution. Table
20 5 shows the amount of the obtained crystal and post-crystal filtration solution. The arsenic content in the product was 19% and the arsenic concentration ratio was lower. Fig. 3 shows the XRD of the obtained crystal. The obtained crystal was Natrojarosite, and crystalline scorodite, which is believed to shows little arsenic elution and be stable, was not obtained. It is thought that the formation of Natrojarosite hampered the

formation of crystalline scorodite. Although the actual form of arsenic in the product is unknown, it is speculated to be in the form of amorphous scorodite.

Incidentally, arsenic elution from the crystal obtained by this synthesis was 4.9 mg/L (TCLP, acetic acid buffer solution having the pH of 5 was used), therefore it was confirmed that the arsenic was unstable. The result also shows that the obtained scorodite was amorphous.

[0044]

Table 5

arsenic acid solution				ferric sulfate (n hydrate)			
amount(g)	23.7			amount(g)	57.3		
	content(%)	number of moles(mol)	(molecular weight)		content(%)	number of moles(mol)	(molecular weight)
T·As	33.8	0.107	74.92	T·As	0.0		
T·Fe	0.0			T·Fe	21.3	0.218	55.85
				S	18.3	0.327	32.070
				Na			

adjusting pH to 1.5 with 46 mL of 25% NaOH solution

scorodite synthesis pH=1.5, 95°C, 24hrs			
amount(ml)	640		
	content(%)	number of moles(mol)	(molecular weight)
T·As	12.5	0.107	74.92
T·Fe	19.0	0.218	55.85
S	16.4	0.327	32.070
Na	10.3	0.288	22.990

crystal			
amount(Dg)	32.0		
	content(%)	number of moles(mol)	(molecular weight)
T·As	19.0	0.081	74.92
T·Fe	29.0	0.166	55.85
S	5.1	0.051	32.070
Na	1.3	0.018	22.990

post-filtration solution			
amount(ml)	1740		
	content(%)	number of moles(mol)	(molecular weight)
T·As	1.02	0.024	74.92
T·Fe	1.93	0.060	55.85
S		0.000	32.070
Na		0.000	22.990

10 [0045]

Comparative Example 2

Ferric sulfate solution (formed by dissolving 57.3 g of ferric sulfate reagent (n hydrate, iron(III) content rate was about 21.3 %) in warm water, 2.0

equivalents of iron(III) based on arsenic) was added to 23.7 g of 60 % arsenic acid solution manufactured by Wako Pure Chemical Industries, Ltd. (the content of arsenic was 33.8 %). Then, the solution was diluted with water to 640 mL. Since the pH of the mixed solution was 0.64, 26.3 mL of 25 % NaOH solution was added to adjust the pH to 1.0. Na concentration in the mixed solution was 5.9 g/L (measured by an ICPAES analyzer, Model No. SPS3100 available from Seiko Instruments Inc.) Then, the solution was heated to 95 °C, during which the amount of the solution was concentrated to 640 mL, and the scorodite synthesis was conducted for 72 hours. During the heating, the amount of the solution was kept to 640 mL by adding water as appropriate to prevent the excessive decrease of the solution due to evaporation. Although the reaction did not progress immediately after the mixture of the sulfuric acid-leached solution and ferric sulfate solution at room temperature, brown precipitation was observed at around 60 °C as the mixture was heated. After the scorodite synthesis, the obtained crystal was filtered and separated into solid and liquid. The crystal was washed with water, and the wash water was added to the post-filtration solution. Table 6 shows the amount of the obtained crystal and post-crystal filtration solution. The arsenic content in the product was 21% and the arsenic concentration ratio was lower. Fig. 4 shows the XRD of the obtained crystal. The obtained crystal was the mixture of Natrojarosite and crystalline scorodite.

Incidentally, arsenic elution from the scorodite obtained by this synthesis was 0.4 mg/L (TCLP, acetic acid buffer solution having the pH of 5 was used), therefore it was confirmed that the arsenic was stable. The result also shows that the obtained scorodite was crystalline.

[0046]

Table 6

arsenic acid solution				ferric sulfate (n hydrate)			
amount(g)	23.7			amount(g)	57.3		
	content(%)	number of moles(mol)	(molecular weight)		content(%)	number of moles(mol)	(molecular weight)
T-As	33.8	0.107	74.92	T-As	0.0		
T-Fe	0.0			T-Fe	21.3	0.218	55.85
				S	18.3	0.327	32.070
				Na			

adjusting pH to 1.0 with 26.3 mL of 25% NaOH solution

scorodite synthesis pH=1.0, 95°C, 72hrs			
amount(ml)	640		
	content(%)	number of moles(mol)	(molecular weight)
T-As	12.5	0.107	74.92
T-Fe	19.0	0.218	55.85
S	16.4	0.327	32.070
Na	5.9	0.164	22.990

crystal			
amount(Dg)	35.9		
	content(%)	number of moles(mol)	(molecular weight)
T-As	21.0	0.101	74.92
T-Fe	27.0	0.174	55.85
S	5.6	0.063	32.070
Na	1.3	0.020	22.990

post-filtration solution			
amount(ml)	1880		
	content(%)	number of moles(mol)	(molecular weight)
T-As	0.04	0.001	74.92
T-Fe	1.23	0.041	55.85
S	4.9	0.287	32.070
Na	1.77	0.145	22.990

[0047]

5 Comparative Example 3

Ferric sulfate solution (formed by dissolving 57.3 g of ferric sulfate reagent (n hydrate, iron(III) content rate was about 21.3 %) in warm water, 2.0 equivalents of iron(III) based on arsenic) was added to 23.7 g of 60 % arsenic acid solution manufactured by Wako Pure Chemical Industries, Ltd. (the content of arsenic was 33.8 %). Then, the solution was diluted with water to 640 mL. Since the pH of the mixed solution was 0.58, 30.5 mL of 25 % NaOH solution was added to adjust the pH to 1.5. Na concentration in the mixed solution was 11.7 g/L (measured by an ICPAES analyzer, Model No. SPS3100 available from Seiko Instruments Inc.). Then,

the solution was heated to 95 °C, during which the amount of the solution was concentrated to 640 mL, and the scorodite synthesis was conducted for 72 hours. During the heating, the amount of the solution was kept to 640 mL by adding water as appropriate to prevent the excessive decrease of the solution due to evaporation.

5 Although the reaction did not progress immediately after the mixture of the sulfuric acid-leached solution and ferric sulfate solution at room temperature, brown precipitation was observed at around 40 °C and the color changed to yellowish brown at around 50 °C as the mixture was heated. After the scorodite synthesis, the obtained crystal was filtered and separated into solid and liquid. The crystal was washed with

10 water, and the wash water was added to the post-filtration solution. Table 7 shows the amount of the obtained crystal and post-crystal filtration solution. The arsenic content in the product was 18% and the arsenic concentration ratio was lower. Fig. 5 shows the XRD of the obtained crystal. The obtained crystal was the mixture of Natrojarosite and crystalline scorodite.

15 Incidentally, arsenic elution from the scorodite obtained by this synthesis was less than 0.1 mg/L (TCLP, acetic acid buffer solution having the pH of 5 was used), therefore it was confirmed that the arsenic was stable. The result also shows that the obtained scorodite was crystalline.

[0048]

Table 7

arsenic acid solution

amount(g)	23.7		
	content(%)	number of moles(mol)	(molecular weight)
T-As	33.8	0.107	74.92
T-Fe	0.0		

ferric sulfate (n hydrate)

amount(g)	57.3		
	content(%)	number of moles(mol)	(molecular weight)
T-As	0.0		
T-Fe	21.3	0.218	55.85
S	18.3	0.327	32.070
Na			

adjusting pH to 1.5 with 30.5 mL of 25% NaOH solution

scorodite synthesis pH=1.5, 95°C, 72hrs

amount(ml)	640		
	content(%)	number of moles(mol)	(molecular weight)
T-As	12.5	0.107	74.92
T-Fe	19.0	0.218	55.85
S	16.4	0.327	32.070
Na	11.7	0.325	22.990

crystal

amount(Dg)	43.1		
	content(%)	number of moles(mol)	(molecular weight)
T-As	18.0	0.104	74.92
T-Fe	28.0	0.216	55.85
S	6.8	0.091	32.070
Na	1.9	0.036	22.990

post-filtration solution

amount(ml)	1650		
	content(%)	number of moles(mol)	(molecular weight)
T-As	0.02	0.000	74.92
T-Fe	0.15	0.004	55.85
S	5.3	0.273	32.070
Na	4.37	0.314	22.990

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A method for manufacturing crystalline scorodite from acidic aqueous solution containing pentavalent As and trivalent Fe, the method comprising a step of adding a basic sodium compound to the acidic aqueous solution such that the sodium concentration in the acidic aqueous solution becomes larger than 0 g/L and equal to or less than 4 g/L.
2. The method for manufacturing crystalline scorodite claimed in claim 1, wherein said basic sodium compound is sodium carbonate, sodium hydroxide, or sodium hydrogen carbonate, or any combination thereof.
3. The method for manufacturing crystalline scorodite claimed in claim 1 or 2, wherein the pH of said acidic aqueous solution is less than 1.0 before the addition of said basic sodium compound and is 1.0 to 1.5 after the addition.
4. The method for manufacturing crystalline scorodite claimed in any one of claims 1 to 3, wherein the trivalent Fe is provided as ferric sulfate.
5. The method for manufacturing crystalline scorodite claimed in any one of claims 1 to 4, wherein said acidic aqueous solution is sulphuric acid-leached solution from electrolytically precipitated copper.

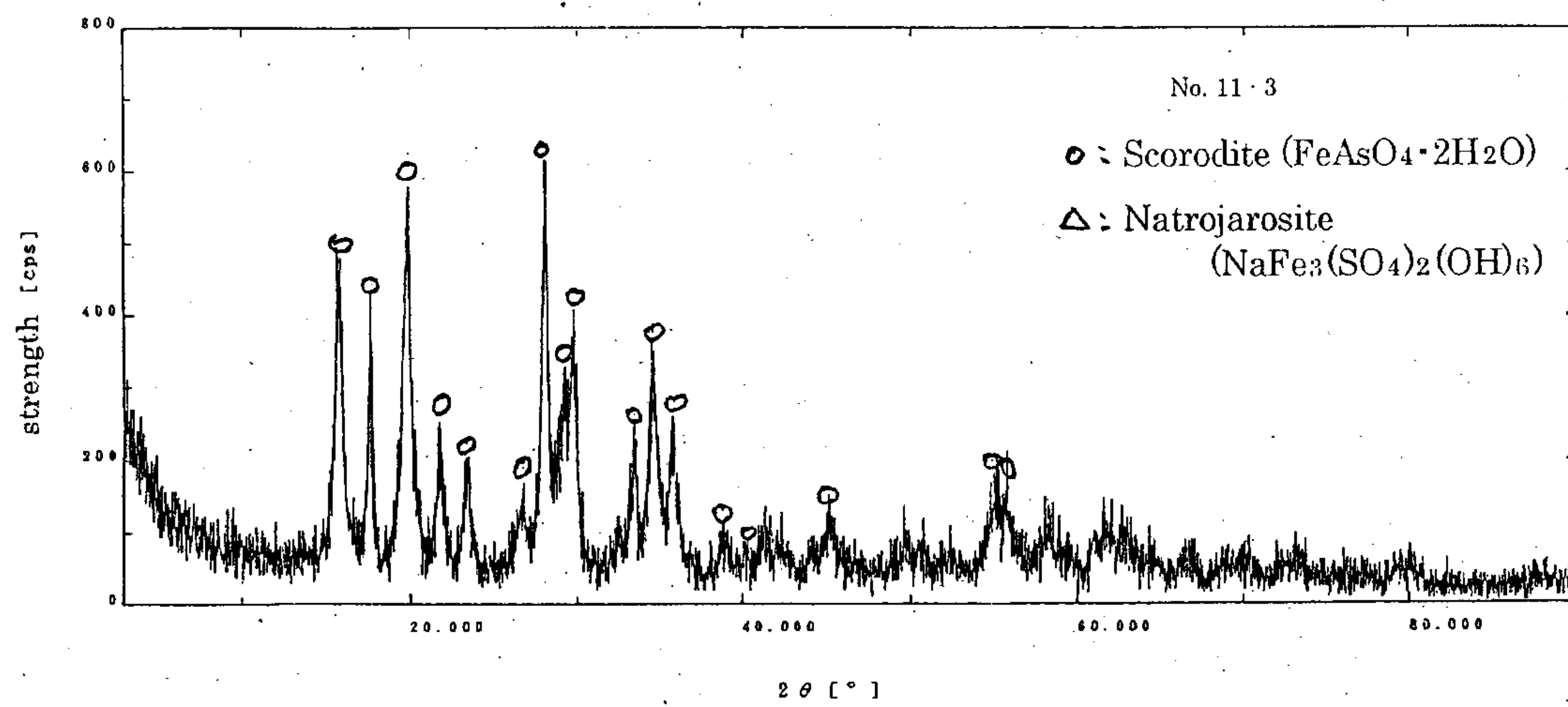


Fig. 1

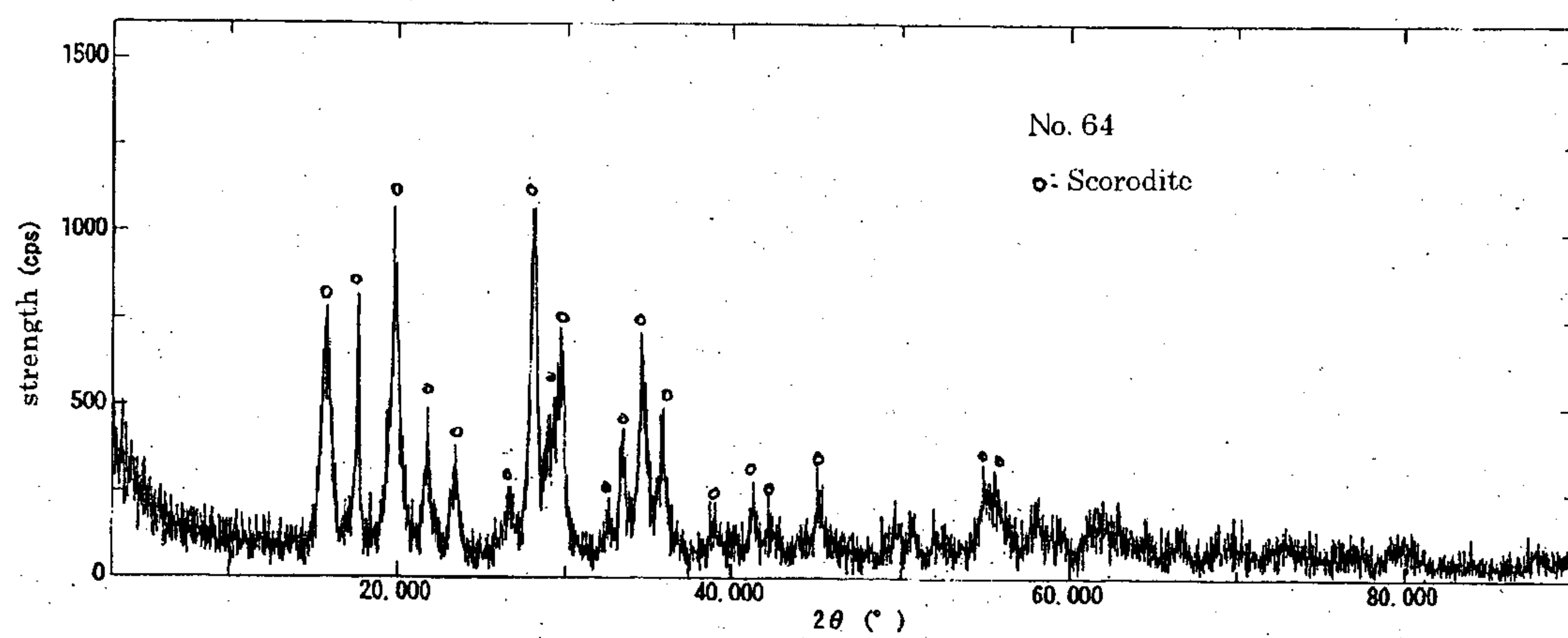


Fig. 2

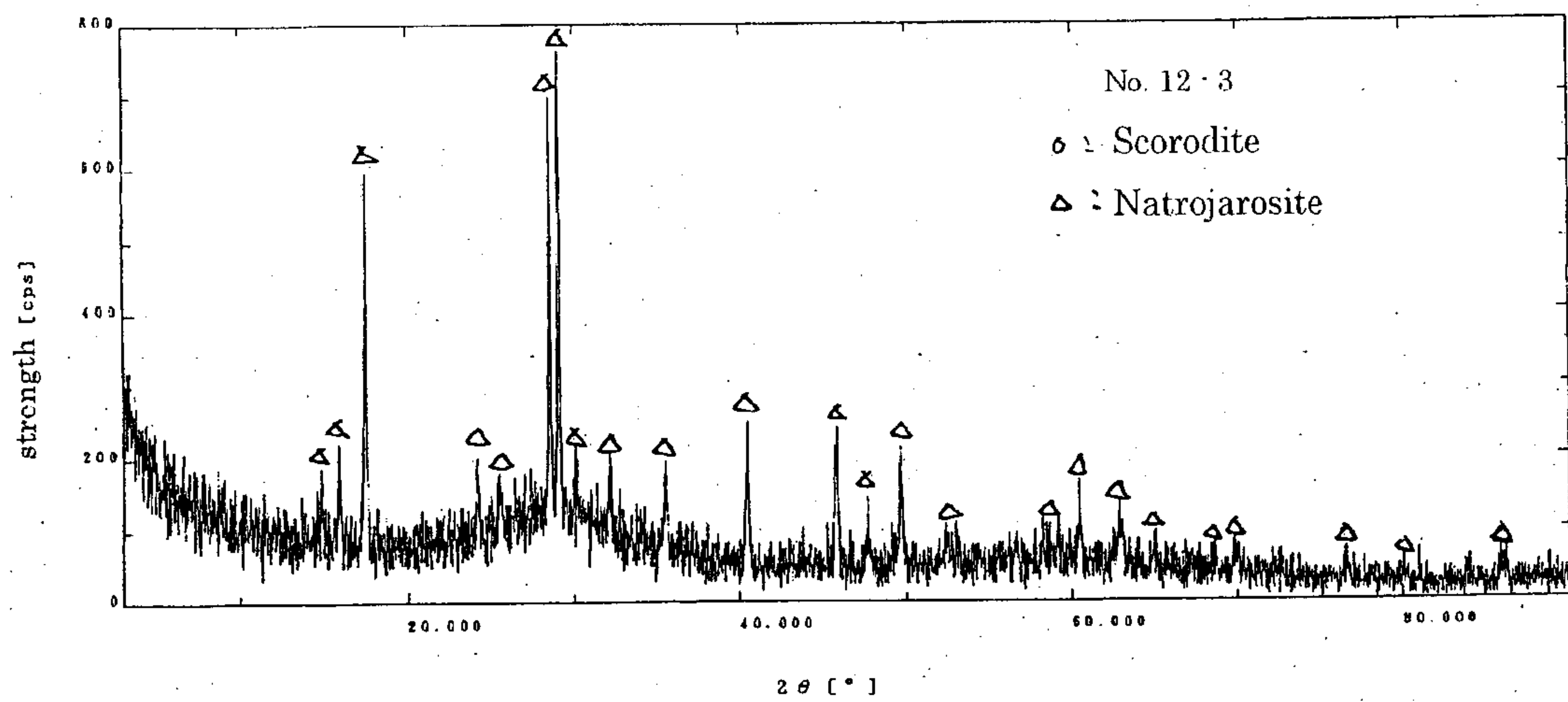


Fig. 3

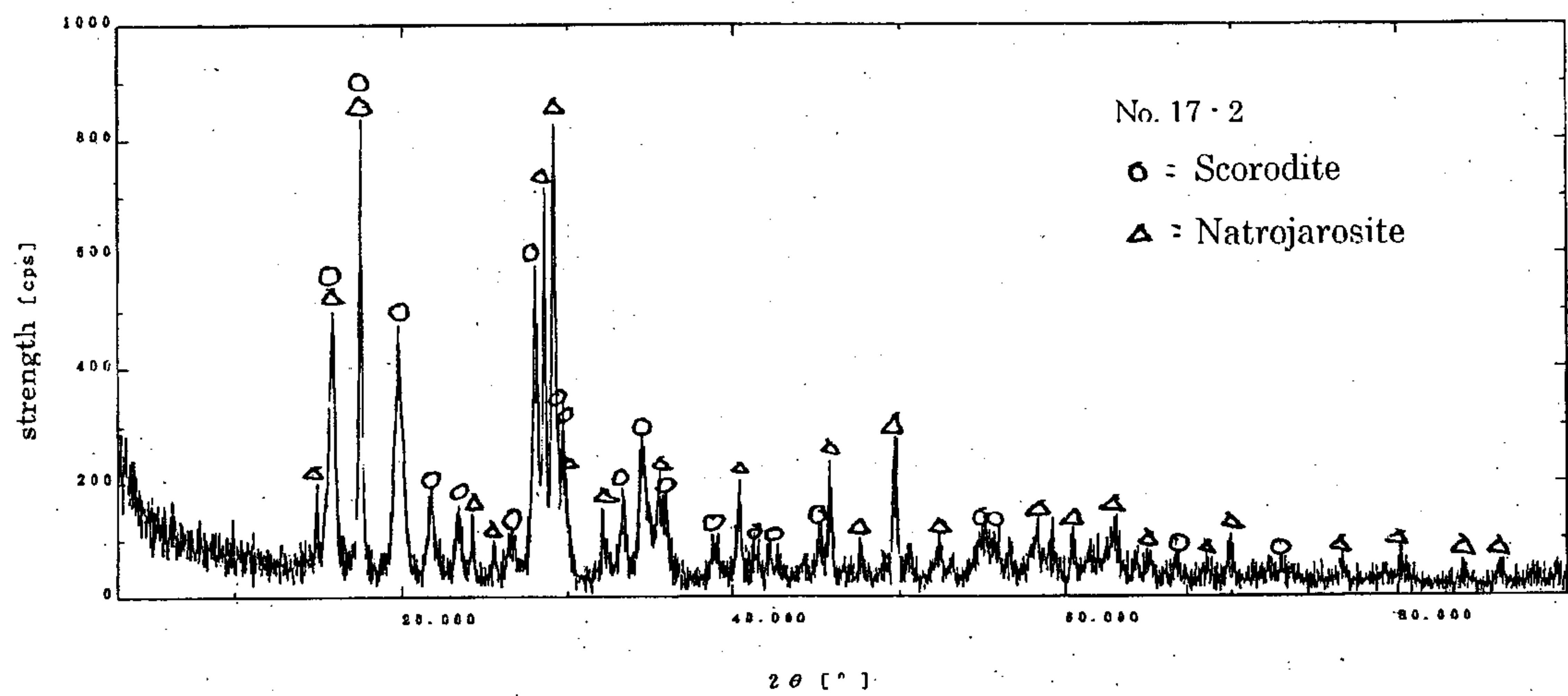


Fig. 4

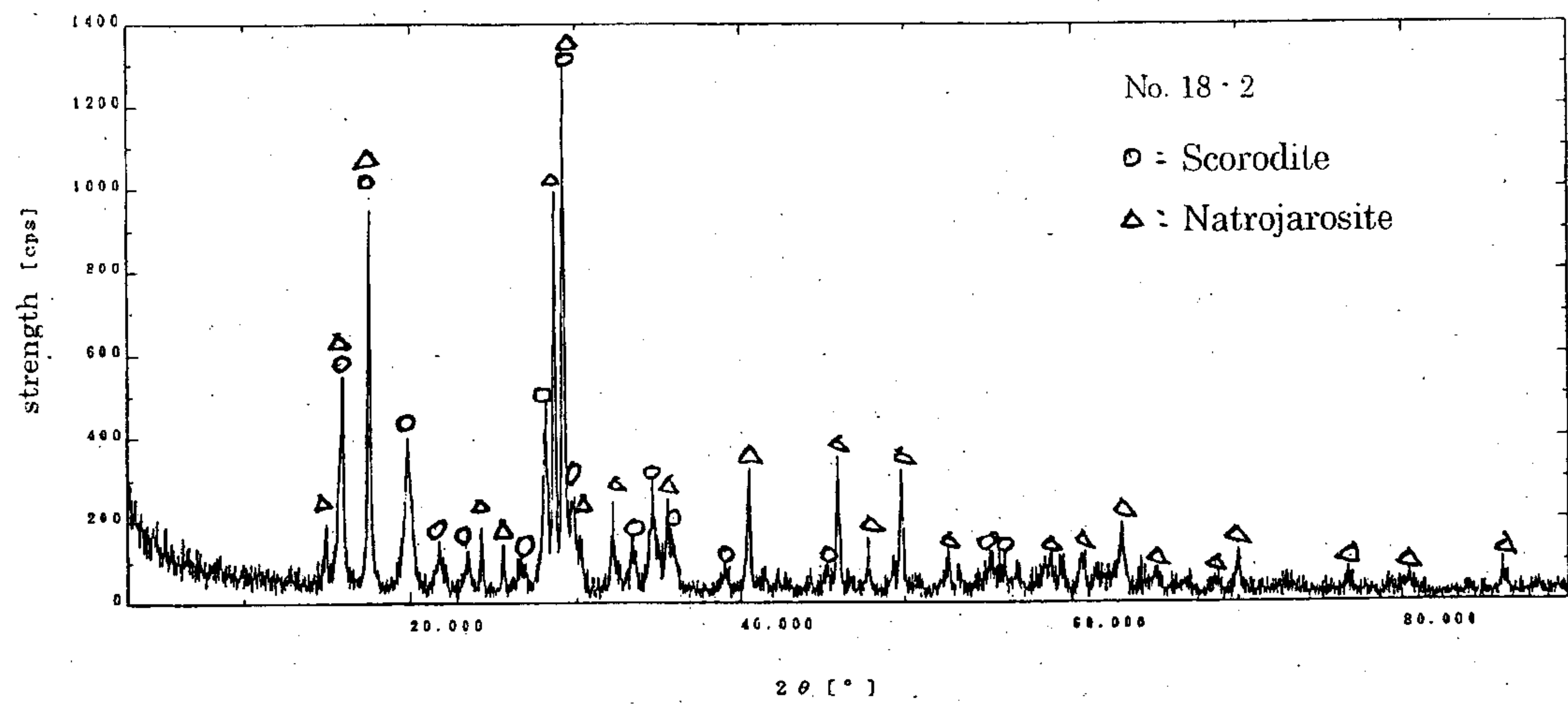


Fig. 5

strength [cps]

